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(54) Copolymers of ethylene

(57) Terpolymers of ethylene having a melt index of between 1 and 500 dg/mn comprise:

88 to 98.7 mol % of units derived from ethylene,

1 to 10 mol % of units derived from at least one ester selected from the alkyl acrylates and methacrylates, said alkyl group having 1 to 6 carbon atoms, and

0.3 to 3 mol % of units derived from maleic anhydride, and having a polydispersity greater than 6.

A process of manufacture is also disclosed. The polymers may be used in the production of film.

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SPECIFICATION

Polymers of ethylene

5 The present invention relates to polymers of ethylene comprising units derived from maleic anhydride and to their application to the manufacture of films.

10 French Patent No. 1,323,379 describes terpolymers of ethylene, an alkyl acrylate and maleic anhydride, of low crystallinity, used as modifiers of petroleum waxes at the rate of 5 to 10% by weight in said waxes, for coating paper.

15 The present invention relates to improved polymers comprising on the one hand ethylene as the main monomer, and on the other hand at least two comonomers, one of which is a (meth)acrylic ester and the other maleic anhydride. Optionally, they may comprise a fourth monomer which is copolymerisable with the first three and they are then called tetra-polymers.

The polymers according to the invention comprise:

25 88 to 98.7% mols of units derived from ethylene, 1 to 10% mols of units derived from at least one ester selected from the alkyl acrylates and methacrylates, said alkyl group having 1 to 6 carbon atoms of carbon.

30 0.3 to 3% mols of units derived from maleic anhydride.

Preferably the polymers have one or more of the following features: melt index (measured according to Standard ASTM D 1238-73) of between 1 and 500 dg/mn; a polydispersity Mw/Mn greater than 6, 35 and/or a Vicat temperature of between 30°C (high content of comonomers) and 85°C (low content).

40 When the polymers according to the invention comprise a fourth comonomer, this may be selected from the α -olefines having 3 to 8 carbon atoms, the monoalkyl maleates and dialkyl maleates in which the alkyl groups have 1 to 6 carbon atoms, vinyl acetate and carbon monoxide, and may be present at the rate of up to 5 mol %, the proportion of ethylene in the tetrapolymer then being reduced correspondingly in relation to the range indicated above.

45 A process of manufacture of the polymers according to the invention consists in copolymerising, in the presence of at least one free radical initiator, a mixture composed of 94 to 99% by weight of 50 ethylene, of 0.7 to 5% by weight of (meth)acrylic ester and of 0.2 to 0.9% by weight of maleic anhydride in a reactor maintained at a pressure of 1,000 to 3,000 bars and a temperature of 170° to 280°C, releasing the pressure, then separating the mixture of 55 monomer and of the polymer formed in the reactor, and finally in recycling to the reactor the mixture of ethylene and of monomers previously separated, the recycled stream comprising from 99 to 99.8% of ethylene and from 0.2 to 1% of (meth)acrylic ester. In 60 the process according to the invention, a separate feed of the fresh ethylene on the one hand and of the comonomers and the recycled ethylene on the other hand may be provided. The introduction of the comonomers into the reactor is preferably effected by 65 placing under pressure, a solution of maleic anhydride in (meth)acrylic ester, mixing this solution with the stream of ethylene and homogenizing said mixture before it enters the reactor. By way of a non-limiting example, the mixing and the homogenization may be effected simultaneously in a device of the Venturi type. Of course, it is possible to consider separating the recycled ethylene and (meth)acrylic ester but such an operation does not provide advantages which compensate for the corresponding increase in the cost of manufacture.

70 Examples of free radical initiators which can be used within the scope of the present invention which may be cited are 2-ethylhexyl peroxydicarbonate, di-tertiary butyl peroxide, tertiary butyl perbenzoate and tertiary butyl 2-ethyl-hexanoate. In a well known manner, it is also possible to use, in the process according to the invention, one or more chain transfer agents, such as hydrogen for example, to regulate and control the characteristics of the 85 polymer and particularly its melt index.

The process according to the invention is carried out in a continuous manner either in an agitated autoclave reactor comprising one or more zones or in a tubular reactor as described, for example, in East 90 German Patent No. 58,387. Situated downstream of the reactor are an expansion valve followed by a separator operating under a pressure of 200 to 500 bars. The process according to the invention may use cooling of the mixture of polymer and of monomers between the expansion valve and the 95 separator, for example in accordance with French Patent No. 2,313,399, by injecting ethylene at a pressure lower than that of the separator, which ethylene may be collected downstream of an exchanger of the 100 recycling circuit.

The polymers according to the invention may be used in numerous applications, either alone or mixed with other materials or polymers. As with the copolymers of ethylene and (meth)acrylic ester, the 105 properties of which they improve, their applications depend on the melt index obtained by the use of the chain transfer agent. They likewise depend on the content of units derived from maleic anhydride. Thus an important application of the polymers 110 according to the invention having a melt index comprised between 1 and 10 dg/mn and comprising from 0.3 to 1% of mols units derived from maleic anhydride consists in the manufacture of films. These films may have a thickness of between 10 and 500 μ m 115 (microns) when they are obtained through a sheet die and from 25 to 200 μ m (microns) when they are obtained by extrusion-blowing. They are used for the manufacture of sachets, food packaging, the wrapping of heavy parcels, and as agricultural films. 120 The extrusion-blowing of these films is effected by means of conventional machines and with a blow-up ratio of between 1 and 3 and a take-off rate which may reach some tens of metres per minute.

The invention will be further described by way of 125 example.

EXAMPLES 1 to 4

130 A cylindrical autoclave reactor is used, comprising three zones each with a volume of 1 litre and equipped with a paddle stirrer. The zones are separated by valve screens. The fresh ethylene compressed by a

first compressor feeds the first zone. The second zone is fed with a homogeneous mixture of ethylene, maleic anhydride (AM) and ethyl acrylate (AE).

Finally a solution of tertiary butyl 2 - ethyl - perhexanoate in a hydrocarbon cut is injected into the third zone. This therefore constitutes the only reaction zone because it brings together the three comonomers and a free radical initiator. Table I, below, shows on the one hand the proportions by weight of maleic anhydride and of ethyl acrylate relative to ethylene in the reaction zone and on the other hand the temperature in said zone. The reactor is maintained at a pressure of 1,600 bars. At the bottom of the third zone of the reactor there is placed an expansion valve allowing the pressure to be reduced to 300 bars. The mixture of the molten polymer on the one hand and the gaseous monomers on the other hand, after having passed through the expansion valve, enters a separating funnel. While the polymer is collected at the bottom of the funnel, the monomers, after passing through a degreasing funnel, are conveyed towards a second compressor. On the other hand, a solution of maleic anhydride in ethyl acrylate is placed under pressure and conveyed towards the inlet to a homogeniser of the Venturi type where it is mixed with the stream of recycled monomers coming from the second compressor. At the outlet from this Venturi device, the mixture of the three monomers is conveyed towards a spiral homogeniser and then transferred to the second zone of the reactor.

At the outlet from the separating funnel, the terpolymer produced is analysed by infra-red spectrophotometry and the proportions in mols of ethyl acrylate units and of maleic anhydride units are determined; they are indicated in Table I below. On the other hand, the melt index of the polymer is determined according to Standard ASTM D 1238-73 and expressed in dg/mn.

Thereafter the following characteristics of the polymer are measured:

density δ , expressed in g/cm³ and determined according to the Standard ASTM D 2839,
number-average molecular weight M_n , determined by gel permeation chromatography,
polydispersity, determined by the same method and equal to the ratio M_w/M_n , M_w being the weight-average molecular weight,

Vicat temperature, expressed in degrees Centigrade and determined according to Standard NF T 51-012 (1).

The results of these measurements are assembled in Table II below.

EXAMPLE 5

The device of the previous examples is used to copolymerise ethylene, maleic anhydride and ethyl acrylate under the following conditions:

Pressure of the reactor: 1,200 bars
Temperature of the reaction zone: 180°C

The composition by weight of the mixture of monomers in the reaction zone, the composition in mols of the terpolymer obtained and its melt index are indicated in Table I below. The polymer is then analysed and characterised by its density, its

molecular weight M_n and its polydispersity, measured as described previously and the values of which appear in Table II below.

EXAMPLE 6

The device of the previous examples is used to copolymerise ethylene, maleic anhydride and butyl methoacrylate (BMA) under the following conditions:

Pressure of the reactor: 1,800 bars
Temperature of the reaction zone: 180°C

The proportions by weight of the comonomers in the reaction zone are as follows:

4.8% BMA, 0.38% MA

The polymer obtained has a melt index of 30 dg/mn (measured according to Standard ASTM D 1238-73).

EXAMPLE 7

The device of the previous examples is used to copolymerise ethylene, maleic anhydride and butyl acrylate (BA) under the following conditions:

Pressure of the reactor: 2,300 bars
Temperature of the reaction zone: 260°C

The proportions by weight of the comonomers in the reaction zone are as follows:

1.3% BA, 0.23 MA

The polymer obtained has a melt index of 2 dg/mn (measured according to Standard ASTM D 1238-73), a Vicat temperature of 65°C and a density of 0.935 g/cm³. Its analysis by infra-red spectrophotometry enables the presence of:

2.0% mols of units derived from butyl acrylate,
0.8% mols of units derived from maleic anhydride to be shown.

EXAMPLE 8

The terpolymer obtained in Example 2 is transformed by extrusion-blowing at a temperature of 140°C into a film with a thickness of 100 μ m (microns), the take-off rate being equal to 2.5 m/mn and the blow-up ratio being equal to 2. The following properties are measured on the film obtained:

Yield strength YS expressed in kg/cm² and determined according to Standard NF T 51-034,
tensile strength TS (expressed in kg/cm²) and elongation at break EB (expressed as a percentage) determined according to Standard ASTM D 882-67.

The following values are found, perfectly balanced in the longitudinal and transverse directions:

YS = 51 kg/cm²
TS = 112 kg/cm²
EB = 540%.

EXAMPLE 9

The terpolymer obtained in Example 1 is transformed into a film with a thickness of 100 μ m, under the same conditions as Example 8. The properties measured on this film are the following:

YS = 59 kg/cm² TS = 100 kg/cm² EB = 450%

TABLE 1

Example	T°C	Reactor		Polymer		Melt Index
		%MA	%EA	%MA	%EA	
1	230	0.25	0.85	0.4	1.3	3.8
2	200	0.31	1.16	0.8	2.1	4.8
3	180	0.30	3.5	1.0	4.7	8.2
4	175	0.84	4.4	2.1	7.7	50
5	180	0.36	3.6	1.0	6.7	200

TABLE 2

Example	1	2	3	4	5
δ	0.930	0.936	0.942	0.960	0.944
Mn	17,500	17,000	15,500	9,500	7,850
Mw/Mn	10.0	7.2	9.0	8.4	73.5
T°Vicat	81	77	51		

CLAIMS

1. A polymer of ethylene having a melt index of between 1 and 500 dg/mn, and comprising:
 - 5 88 to 98.7 mol % of units derived from ethylene, 1 to 10 mol % of units derived from at least one ester selected from the alkyl acrylates and methacrylates, said alkyl group having 1 to 6 carbon atoms, and
 - 10 0.3 to 3 mol % of units derived from maleic anhydride, and having a polydispersity greater than 6.
2. A polymer as claimed in Claim 1, characterised in that its Vicat temperature is between 30°C and 85°C.
3. A polymer as claimed in one of Claims 1 and 2, characterised in that it comprises up to 5 mol % of units derived from a fourth comonomer selected from the α -olefines having 3 to 8 carbon atoms, monoalkyl maleates and dialkyl maleates, the alkyl groups of which have from 1 to 6 carbon atoms, vinyl acetate and carbon monoxide.
4. A polymer as claimed in one of Claims 1 to 3, characterised in that it comprises from 0.3 to 1 mol % of units derived from maleic anhydride and in that its melt index is between 1 and 10 dg/mn.
5. A polymer as claimed in one of Claims 1 to 4, characterised in that the ester is butyl methacrylate.
6. A polymer as claimed in one of Claims 1 to 4, characterised in that the ester is butyl acrylate.
7. A polymer as claimed in one of Claims 1 to 4, characterised in that the ester is ethyl acrylate.
8. A process for the manufacture of a terpolymer as defined in claim 1, consisting in copolymerising, in the presence of at least one free radical initiator, a mixture composed of 94 to 99% by weight of ethylene, of 0.7 to 5% by weight of at least one (meth)acrylic ester and from 0.2 to 0.9% by weight of maleic anhydride in a reactor maintained at a pressure of 1,000 to 3,000 bars and a temperature of 170° to 280°C, releasing the pressure, then separating the mixture of monomer and of the terpolymer formed

in the reactor and finally in recycling to the reactor the mixture of ethylene and monomers previously separated, characterised in that the mixture recycled to the reactor comprises from 99 to 99.8% of ethylene and from 0.2 to 1% of (meth)acrylic ester.

9. A process as claimed in claim 8, characterised in that the free radical initiator is selected from 2-ethylhexyl peroxydicarbonate, di-tertiary butyl peroxide, tertiary butyl perbenzoate and tertiary butyl 2-ethyl-perhexanoate.

10. The application of a terpolymer as claimed in claim 8 to the manufacture of films having a thickness of between 10 and 500 μ m (microns).

11. A method of producing a polymer of ethylene as defined in claim 1, substantially as hereinbefore described.

12. A polymer produced by a process as claimed in claim 9, 10 or 11.

13. A polymer of ethylene, substantially as hereinbefore described with reference to any one of the foregoing examples 1 to 5.

14. A film comprising a polymer as defined in any one of claims 1 to 7, 12 and 13.

15. A film as claimed in claim 14, having a thickness of from 10 to 500 microns.

16. The features hereinbefore disclosed or their equivalents in any novel combination.

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